PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PC3-008	**FOR FURTHER ACTION** See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US 02/30729	International filing date *(day/month/year)* 27.09.2002	Priority date *(day/month/year)* 28.09.2001
International Patent Classification (IPC) or both national classification and IPC C07C17/10		
Applicant PCBU SERVICES INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 8 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 19 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand 23.04.2003	Date of completion of this report 20.02.2004
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Seufert, G Telephone No. +49 89 2399-8330

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US 02/30729

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

2-4, 12, 14-25, 27, 29-36, 38-51 as originally filed

1, 5-11, 13, 26, 28, 37, 52 received on 06.02.2004 with letter of 06.02.2004

Claims, Numbers

1-63 received on 06.02.2004 with letter of 06.02.2004

Drawings, Sheets

1/7-7/7 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

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5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to thi. report.)

see separate sheet

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application,

☒ claims Nos. 20-63

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):

☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinior could be formed.

☒ no international search report has been established for the said claims Nos. 20-63

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide anc or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the Standard.

☐ the computer readable form has not been furnished or does not comply with the Standard.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-19
	No:	Claims	
Inventive step (IS)	Yes:	Claims	19
	No:	Claims	1-17
Industrial applicability (IA)	Yes:	Claims	1-19
	No:	Claims	

2. Citations and explanations

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see separate sheet

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT - SEPARATE SHEET

International application No. PCT/US02/30729

Reference is made to the following documents:

D1 US-A-5043491
D2 US-A-5068472
D3 EP-A-539989
D4 US-A-6018083
D5 US-A-5057634

III. Non establishment of opinion

1. According to Rule 66.1e the International Preliminary Examination Authority is not required to carry out an examination on subject-matter for which no search report as been established.
   An objection of lack or unity has been raised by the International Search Authority together with an invitation to pay additional search fees. These search fees have not been paid and therefore the search report has been established only for the first invention. As a consequence only the first invention is subject of the international preliminary examination.
   The amended claims 1-63 do not overcome the objection of lack of unity. The first invention is reflected in claims 1-19. Thus, only the subject-matter of claims 1-19 has been examined. Amended claim 20 is not a dependent claim, contrary to the applicant's observations submitted with the dependent claims. It was also not included in the searched subject-matter of the first invention.

2. The amendments
   (a) "different from the first temperature" and
   (b) "C-3 reactant comprising one or more..."
   have been considered to go beyond the disclosure as filed (rule 70.2 (c) PCT). The International preliminary examination authority could not find a basis in the appplication for the amendment (a). At various places in the application it is mentioned that the second temperature is higher than the first (see for examples description page 8, lines 27-28, page 11, lines 9-10 and 15). However, the expression "different from the first temperature" also includes the possibility that the second temperature is lower than the first.
   With regard to the definition of the C-3 reactant, a basis for a "C-3 reactant

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comprising one or more..." could not be found in the application as filed. Whereever the C-3 reactant is mentioned in the application as filed, it is clear that it refers to a C-3 compound or mixtures of C-3 compounds. The term comprising means that it can contain other compounds as well.
Consequently, the present report has been stablished as if this amendments had not been made, which effectively means amendment (a) has been completely disregarded and for amendment (b) the original supported disclosure of "non perhalogenated hydrocarbons having three carbon atoms" as been considered.

Furthermore it seems that also some of the amendments in the description are not merely corrections of clerical or typographical errors, for example the introduction of "exemplary" at various places, the introduction of "one or more of high temperature reaction conditions" on page 11, line 3 or "can be prepared" instead of "were prepared" on page 13, line 25.

V. Reasoned statement under Art. 35(2) PCT with regard to novelty, inventive step and industrial applicability

Novelty

Claim 1 of the present application refers to a method for the preparation of 2,2-dichloro-1,1,1,3,3,3-hexafluoropropane ($CF_3CCl_2CF_3$, CFC-216aa) comprising contacting non perhalogenated hydrocarbons having 3 carbon atoms with chlorine and HF in the presence of a first catalyst at a first temperature to form a C-3 product comprising a C-3 perhalogenated compound, wherein the first catalyst comprises chromium and the first temperature is less than 450°C and contacting the C-3 product with HF in the presence of a second catalyst at second temperature to form CFC-216aa.

Document D1, which may be considered as the most relvant prior art discloses the chlorofluorination of a member of the group of propane, propene or partially halogenated C-3 hydrocarbons with Cl_2 and HF in the presence of a metal catalyst at a first temperature between 200 and 460°C (D1, tabe I) to produce $CF_3CCl{=}CCl_2$. This product is then chlorofluorinated at a second temperature between 300 and 500°C to produce $CF_3CClFCF_3$. However, CFC-216aa is also

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produced and in rather high amounts especially at around a temperature of 400°C (see D1, steps (a) and (b), column 3, lines 19-60, column 8, line 48 - column 9, line 6, fig.). D1 also explicitly discloses the use of a chromium catalyst as the first catalyst in combination with a temperature of 450°C.
For the mere formal reason that the combination of a chromium catalyst with temperatures below 450°C is not explicitly mentioned in D1 the independent claim 1 and the dependent claims 2-19 appear to meet the requirement of Art. 33(2) PCT.

Inventive step

The technical advantages of the presently claimed process are the low amount of undesirable isomers, especially $CF_3CF_2CF_3$ (FC-218). However, document D1 also shows the formation of low amounts of $CF_3CF_2CF_3$, see D1, fig.

The problem to be solved by the present invention is considered as providing an altemative chlorofluorinating process.

The problem has been solved by the claimed process (see application).

However, the limitation to the use of a chromium catalyst at a temperature below 450°C in the first chlorofluorination step may render the subject-matter of claim 1 novel over D1 but it does not render it inventive, contrary to the applicant's observation. D1 already discloses a two step chlorofluorination process. The temperature of the first reaction step overlaps broadly with the presently claimed temperature (in most examples it is also below 450°C) and metal catalysts in general have been considered suitable in the chlorofluorination process of D1. The use of a chromium catalyst at a temperature below 450°C is thus not considered to be imventive. Furthermore, D1 discloses in example 13 the use of a chromium catalyst at a temperature <u>of 450°C</u>, which was originally included in the scope of claims. All variants covered by a claim are initially regarded as equivalent. By incorporating a prior art process the applicant has presented his presently claimed process as equivalent to that of the prior art. The claimed process is thus not inventive (Art. 33(3) PCT).

Furthermore, the subject-matter of claim 2 and 3 is not considered as involving an

inventive step (Art. 33(3) PCT) for the following reasons.
The reaction of CFC-216 with HF in the presence of a catalyst to form 2-chloro-1,1,1,2,3,3,3 heptafluoropropane (CFC-217ba) as well as the reaction of CFC-217ba with H_2 to HFC-227ea are well known reactions in the prior art (see D2 or D3). The subject-matter of claims 2 and 3 are therefore merely an association of known steps funtioning in the their normal way and not producing any non-obviuos working interrelationship. No inventive skills are necessary.

Dependent claims 5-17 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step, the reasons being as follows: These features are known in the prior art (see D1-D3).

The subject-matter of claim 4 is not considered to be inventive. It appears that the claimed stability is only achieved at a certain level of water in the hydrode-halogenation reaction (see application pages 40-42 and fig. 7).

The subject-matter of the dependent claim 19 appears to satisfy the requirement of Art. 33(3) PCT.

Industrial applicability

There are no objections with regard to the industrial applicability of the subject-matter of claims 1-19.

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MATERIALS AND METHODS FOR THE PRODUCTION AND PURIFICATION OF CHLOROFLUOROCARBONS AND HYDROFLUOROCARBONS

FIELD OF INVENTION

The present invention is directed to production methods, as well as, synthetic and separation methods. More particularly, the present invention is directed to methods for manufacturing selective isomers of chlorofluorocarbons and hydrofluorocarbons from aliphatic, olefinic or partially halogenated hydrocarbons.

BACKGROUND OF THE INVENTION

Since the beginning of global warming concerns, chlorofluorocarbon manufacturers have had to produce compounds that perform substantially the same as fully halogenated chlorofluorocarbons without the adverse environmental impact. Only through the introduction of these new compounds have their environmental impact been completely understood. In certain instances, some of these new compounds have been removed from the marketplace. These types of issues make the flooding agent, extinguishant, propellant and refrigerant production industry a dynamic and ever-changing marketplace where processes for the production of chlorofluorocarbons and fluorocarbons are advancing quickly to accommodate both environmental as well as economical requirements.

Some useful compounds in this area include both saturated and unsaturated fluorocarbons, such as 1,1,1,2,3,3,3-heptafluoropropane (CF_3-CFH-CF_3, HFC-227ea), 1,1,1,2,2,3,3-heptafluoropropane (CF_3-CF_2-CHF_2, HFC-227ca) and hexafluoropropane (hexafluoropropylene, HFP, CF_3-CF=CF_2, FC-1216). One well known method of synthesizing these compounds begins with the chlorofluorination of propane, propylene or partially halogenated C-3 hydrocarbons with hydrogen fluoride (HF) and chlorine (Cl_2) in the presence of a metal-containing solid catalyst. Examples of this chlorofluorination step can be found in U.S. Patents 5,057,634 and5,043,491 to Webster. As taught by Webster, the chlorofluorination step produces a number of saturated perhalogenated chlorofluorocarbons, including: (A) $C_3Cl_5F_3$; (B) $C_3Cl_4F_4$; (C) $C_3Cl_3F_5$; (D) 1,2-dichlorohexafluoropropane (CF_3-CClF-$CClF_2$, CFC-216ba); (E) 2,2-dichlorohexafluoropropane (CF_3-CCl_2-CF_3, CFC-216aa); (F) 1-

Still another process for separating halogenation reaction products is provided wherein the reaction products are combined with water and cooled to a sufficient temperature to form a gas phase and top and bottom liquid phases. According to one embodiment, the gas phase contains primarily C-3 chlorofluorinated compounds having at least six fluorine atoms, the top liquid phase is primarily an aqueous liquid phase and the bottom liquid phase contains C-3 chlorofluorinated compounds having less than six fluorine atoms.

An additional process according to this invention provides for separating C-3 chlorofluorinated compounds from a halogenation reaction product. One embodiment of this invention includes the adjustment of a halogenation reaction product to a sufficient temperature to separate the reaction product into three phases: an upper gas phase and top and bottom liquid phases, wherein the upper gas phase contains primarily HCl, the top liquid phase contains HF and the bottom liquid phase contains essentially acid-free C-3 chlorofluorinated compounds.

In still another process of the present invention methods are provided for synthetically increasing the isomeric purity of a mixture. According to one embodiment, an isomeric mixture of C-3 chlorofluorinated compound isomers is heated in the presence of a catalyst to a sufficient temperature to increase the isomeric purity. In a more specific embodiment, the C-3 chlorofluorinated compound isomers are CFC-217ba and CFC-217ca.

In still another embodiment of the present invention a process is provided for selectively halogenating isomers within an isomeric mixture. In a particular embodiment, the isomeric mixture is exposed to Cl_2 in the presence of a catalyst at a sufficient temperature to halogenate at least one isomer. Preferably the isomeric mixture includes the isomers HFC-227ea and HFC-227ca.

The above and other embodiments, aspects, alternatives and advantages of the present invention will become more apparent from the following detailed description of the present invention taken in conjunction with the drawings.

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DESCRIPTION OF THE FIGURES

Figure 1 is a schematic representation of one embodiment of the present invention.

Figure 2 is a graphical representation of the isotherms observed during the processes of the present invention.

Figure 3 is a block diagram of an embodiment of the present invention.

Figure 4 is a block diagram of an embodiment of the present invention.

Figure 5 is a block diagram of an embodiment of the present invention.

Figure 6 is a block diagram of an embodiment of the present invention.

Figure 7 is a graphical representation of catalyst life observed according to an embodiment of the present invention.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to Fig. 1, in one embodiment this invention provides processes for the production of chlorofluoropropanes and fluoropropanes from aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms. Other embodiments of this invention provide specific processes for hydrodehalogenation, as well as, isomer and reaction product purification. Selected embodiments of this invention will be described in turn beginning with the broad chemical process steps used to produce selected chlorofluorocarbons and fluorocarbons.

In part, this invention stems from the discovery that the majority of the isomer in the final chlorofluorocarbon or hydrofluorocarbon product originates as an undesired isomer which forms in the initial reactions. This isomer and its downstream counterparts are passed to subsequent reactions undergoing the same chemical transformation as the desired isomeric material. Fortunately, CFC-216ba and its downstream counterparts, have different reaction profiles allowing for their reduction with each subsequent step. Unlike CFC-217ca and HFC-227ca, CFC-216ba is not a "dead end" isomer. A majority of this material is directly converted to the desired isomer CFC-217ba in subsequent steps performed in accordance with the present invention.

Without being confined to any theory, the formation of the undesired isomer takes place in these early reactions by the premature fluorination of the geminal C-2 carbon of aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms. The production of CFC-216ba is but just one example of this type of chemistry.

Referring now to Fig. 2, formation of excess amounts of CFC-216ba during halogenation has been observed when the reaction is allowed to exotherm excessively. The large amounts of energy released during this exotherm are probably the ultimate reason for

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excess CFC-216ba isomer formation. When these types of conditions are allowed to prevail, ratios as low as 2:1 CFC-216aa:CFC-216ba can be observed in these early reaction streams.

One way to control this phenomenon can be to carefully operate the initial halogenations so as to avoid uncontrolled exotherms. The reactor used according to the present invention has the ability to use cool heat transfer oil and includes conventional chemical and engineering controls to insure suppression of exotherms. In another aspect of the present invention, HF can be replaced as the main diluent for the reaction. Figs. 3–4 show a schematic flow diagram for a process according to the present invention that includes a two temperature zone chlorofluorination of a C-3 reactant selected from propane, propylene, partially halogenated C-3 acyclic hydrocarbons, and mixtures thereof, with hydrogen fluoride and chlorine in the presence of a chlorofluorination catalyst. The process is highly selective in the production of CFC-216aa, without the formation of any significant amount of FC-218 (0 to less than 0.5 percent by weight). The high yield and selectivity of the process of the present invention in the synthesis of CFC-216aa is very advantageous for the subsequent production of HFC-227ea as discussed below.

The present invention provides, in one aspect, two step processes for efficiently producing CFC-216aa. The chemical steps can include the sequential replacement of hydrogen with chlorine and the subsequent partial replacement of chlorine with fluorine atoms. Multiple products may be formed with intermediate fluorinated materials being the majority. Careful temperature control may minimize by-product formation. Typical reaction products may include C-3 molecules with 2 to 7 fluorine atoms, the rest being chlorine. The cracking of the C-3 backbone to form C-1 and C-2 materials as undesired impurities has also been observed. According to one embodiment, the output of this reactor can be fed directly into a subsequent reactor as shown in Fig. 4, which is run at a higher temperature. Individual reactants may be fed under flow control to vaporizer(s) 14, as shown in Fig. 3. The vaporized chlorine and HF are mixed and fed into a superheater. It has been determined that careful mixing of the reactants and temperature regulation may help to control reaction exotherms and lack of control may lead to the formation of undesired by-products arising from cracking the C-3 backbone.

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The predominant reaction occurring in exemplary chlorofluorination Steps I and II may be summarized, as follows, with high selectivity in the production of CFC-216aa:

$$CH_3CH_2CH_3,\ CH_3CH{=}CH_2 \text{ and/or } C_3H_yX_z{+}HF{+}Cl_2 \rightarrow \text{CFC-216aa}{+}HCl$$

$$(X{=}\text{halogen};\ y{=}0\text{-}8,\ z{=}8\text{-}y;\ \text{or } y{=}0\text{-}6,\ z{=}6\text{-}y)$$

According to one aspect, the process includes a first step, wherein C-3 reactants selected from the group consisting of aliphatic, olefinic or partially halogenated hydrocarbons having at least three carbon atoms are contacted with Cl_2 and HF in the presence of a metal containing catalyst. As illustrated in Fig. 3, this reaction is preferably performed in the gas phase by the careful mixing of C-3 reactants with a mixture of hydrogen fluoride (HF) and chlorine (Cl_2) in the presence of a metal containing catalyst at a sufficient temperature to form perhalogenated compounds.

In one embodiment of the present invention, the C-3 reactant is selected from the group consisting of aliphatic, olefinic and/or partially halogenated hydrocarbons. The C-3 reactant may be premixed with hydrogen fluoride, and then mixed with chlorine before entering chlorofluorination reactor 16 containing a fixed bed of metal containing catalyst.

Aliphatic hydrocarbons having at least three carbon atoms are known to those skilled in the art to be alkanes, hydrocarbons characterized by a straight or branched carbon chain. These types of compounds include propane. Olefinic hydrocarbons having at least three carbon atoms are known to those having ordinary skill in the art to be unsaturated aliphatic hydrocarbons having at least one double bond. These types of compounds include propene. Partially halogenated hydrocarbons having at least three carbon atoms are known to those having ordinary skill in the art as aliphatic or olefinic hydrocarbons wherein one or more hydrogens have been replaced by halogens.

According to one embodiment of the present invention, the HF and C-3 reactants are premixed before being combined with the chlorine gas and conveyed into a chlorofluorination reactor. It is preferred to premix (dilute) the C-3 reactant with the hydrogen fluoride reactant prior to combining the HF/C-3 gas reactants with the chlorine gas reactant in order to minimize the potential reaction of the C-3 reactant, e.g., propane and/or propylene with concentrated chlorine gas. Accordingly, at least one of the C-3 reactant or the chlorine, preferably both the C-3 reactant and chlorine, may be diluted with hydrogen fluoride prior to combining the C-3 reactant with the chlorine gas.

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In one embodiment of the present invention the HF is anhydrous. It has been determined that recycled or reagent grade HF may used. The type of HF used to perform this aspect of the invention is not critical and specific types and qualities will be recognized by those skilled in the art. The Cl_2 likewise is a matter of choice to those having skill in the art. In one embodiment, technical or pure-grade anhydrous Cl_2 is utilized.

The halogenation of aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms is a highly exothermic reaction which may be controlled through the use of excess quantities of hydrogen fluoride, a diluent, or an external heat transfer medium together or in combination, to absorb the heat evolved and to maintain temperature control of the mixture.

To reduce the impact of exotherms, preferably, a stoichiometric excess of hydrogen fluoride may be maintained in order to minimize decomposition of the C-3 reactant to C-1 and C-2 by-products, and the formation of the less desired CFC-216ba. Preferably, about 6 to about 64 moles of HF per mole of C-3 reactant may be utilized. It is preferred to provide an excess of chlorine gas as well, preferably about 8 to about 10 moles of Cl_2 per mole of C-3 reactant. However, an excess of Cl_2 is not required. In a preferred embodiment, the ratio of Cl_2 to C-3 reactants can be about 8.2:1. The molar ratio of HF to Cl_2 may be from about 0.75:1 to about 8:1. Preferably, the molar ratio of HF to Cl_2 may be about 4:1. Moreover, in another embodiment, a diluent may be added to the reaction to decrease undesired isomer and formation of cracking materials.

Preferably, the chlorofluorination reactor 16 used to perform this invention may be maintained at a reaction pressure of about 0 psig to about 750 psig, preferably about 0 psig to about 750 psig and at a temperature in the range of about 150°C to about 450°C, and preferably about 220°C. Residence time in chlorofluorination reactor 16 may be in the range of about 0.5 seconds to about 30 seconds and preferably about 5 to about 10 seconds. An exemplary reaction mixture exiting Step I shown in Fig. 3 is rich in $C_3Cl_4F_4$ and $C_3Cl_3F_5$, but may also contain CFC-216aa and many other under fluorinated compounds. In an exemplary aspect, reaction products of this first step are conveyed directly to Step II, as shown in Fig. 4. However, it is recognized that the reaction products of Step I, as shown in Fig. 3, may be further purified or supplemented prior to continuing on to Step II. A main goal in Step II can be the selective fluorination of under-fluorinated compounds to the desired isomer CFC-216aa.

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In the illustrated embodiment, the second step in this process may replace all of the terminal chlorine substituents with fluorine to produce CFC-216aa. According to one aspect of the present invention, this is accomplished through the use of one or more of high temperature reaction conditions, excess HF, and a metal containing catalyst.

As shown in Fig. 4, the Step I reaction stream is directly fed into a superheater 24. Optimally, this stream is then fed to Step II reactor 26. Again, as before in Step I, careful temperature regulation can be used to control the reaction.

The second reaction can take place either in the same reactor as exemplary Step I or, preferably, in a second reactor. The second reaction can be carried out at a higher temperature than the first reaction with a stoichiometric excess of hydrogen fluoride. According to one embodiment, a stoichiometric excess of chlorine can be used to ensure chlorofluorination of the first reaction products.

Reactor 26 can be a fixed-bed reactor having a metal containing catalyst, maintained at a reaction pressure of about 0 psig to about 750 psig and preferably about 100 psig, and at a temperature higher than the temperature required in exemplary Step I. Step II may occur at a temperature ranging from about 300°C to about 550°C, and preferably at about 470°C. It is preferred that the molar ratio of reactants in Step II, should be maintained at about 6 to about 64 moles of hydrogen fluoride per mole of perhalogenated compounds. As in Step I, the source and quality of anhydrous HF used in Step II is not critical. It is to be understood by those skilled in the art that anhydrous, recycled, and/or differing grades of HF can be used in Step II. As in Step I, a diluent may be added to control exotherms and increase isomeric yield.

The metal containing catalyst used in Step I or Step II can be any known catalyst useful for reacting C-3 reactants or perhalogenated compounds with HF and/or Cl_2, including those described in U.S. Patent Nos. 5,177,273 and 5,057,634 to Webster, hereby incorporated by reference. These catalysts include catalysts consisting essentially of chromium; catalysts consisting essentially of chromium oxide in combination with a support (e.g. refractory oxide); catalysts consisting essentially of chromium oxide modified with up to about 10 percent by weight based upon the weight of chromium in the catalyst of metal selected from the group consisting of manganese, iron, cobalt, nickel, copper, zinc, other metals and mixtures thereof; and catalysts consisting essentially of chromium oxide in combination with the refractory oxide and modified with up to about 10 percent by weight based upon the

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under reaction conditions is considered an equivalent procedure within the scope of this invention.

In this and the other reaction sequences, reaction with HF includes either high temperature vapor phase reaction or lower temperature reaction in the presence of a liquid phase catalyst such as $SbCl_5/HF$ or SbF_5; the vapor phase process is preferred.

Two metal containing catalysts that have been found to be particularly useful for the chlorofluorination reactions include:

(1) $FeCl_3$ on a support, particularly active carbon, that is dried and then fluorinated, e.g., with HF, preferably an HF/N_2 mixture, with or without O_2, at about 200°C to about 270°C and then treated with HF, with or without O_2 or Cl_2 activation, within the range of about 270°C to about 320°C. It is preferred that the percent by weight of $FeCl_3$ in the metal containing catalyst be in the range of about 2% to about 36% by weight on a catalyst support, which is preferably activated carbon, preferably at about 5% to about 10% by weight $FeCl_3$. It is useful to fluorinate the metal containing catalyst for a period of at least about 2 hours, preferably about 2 to about 16 hours, more preferably about 8 hours, gradually increasing the temperature within the rage of from about 200°C to at least the chlorofluorination reaction temperature, e.g., up to about 320°C; and

(2) $CrCl_3$, particularly chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) on a support, particularly active carbon, that is dried and then fluorinated, e.g., with hydrogen fluoride gas (HF), in the same manner as fluorination of the $FeCl_3$ catalyst with or without O_2 or Cl_2 activation.

Non-limiting examples 1, 2 and 3 demonstrate the preparation of catalysts suited for the present invention and non-limiting example 4 demonstrates the activation of catalyst suited for this invention.

Generally, all fluorination catalyst can be prepared by mixing appropriate amounts of the selected metal salt and support (if necessary) in DI Water. This mixture may be allowed to stand for approximately 0.5 hour and the excess water can be filtered off by vacuum filtration. The resulting solid may then be dried overnight in a gravity oven at 115°C and then charged to the reaction tubes where it can be further dried at 150°C with a inert gas purge and then activated with HF before the reaction feeds are started.

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Table 6. Chlorofluorination Organic Phase Removed from HF According to a Process of the Present Invention

	Area % Cl_2	Area % HF	Area % HCl	Area % Organic
Separated Organic Phase	1.21	0.3872	0.6097	97.79

Table 7. Halogenated Organics Separated from HF According to the Present Invention

Halogenated Organics	Percentage of Total Organics
CCl_3F-$CClF_3$	not detected
Lights	0.05
$C_3Cl_2F_6$	64.59
$C_3Cl_3F_5$	11.82
$C_3Cl_4F_4$	5.75
Heavies	3.65

As this example demonstrates the organic phase, once separated according to an embodiment of the present invention, is essentially acid-free. This allows for the immediate isolation of specific chlorofluorination reaction products without the need for costly and inefficient distillation. Moreover, Table 7 demonstrates that other halogenated organics can be separated from HF, according to the present invention. These chlorofluorination reaction products can be isolated according to another process of the present invention as herein described next.

Another process according to the present invention is the separation of the C-3 chlorofluorinated compounds having at least six fluorine atoms from C-3 chlorofluorinated compounds having less than six fluorine atoms. This separation process is extremely useful in order to maintain the compound purity of chlorofluorinated compounds sought to be produced.

According to one embodiment of the present process, a solution comprising C-3 chlorofluorinated compounds having at least six fluorine atoms and C-3 chlorofluorinated compounds having less than six fluorine atoms is provided. This solution is derived from a reaction product or a refined reaction product of a chlorofluorination reaction or the phase separation or distillation product after a chlorofluorinated reaction. In one embodiment of the present Invention the C-3 chlorofluorinated compounds having at least six fluorine atoms comprises CFC-216aa. However, this invention is not limited to the source of this mixture.

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chlorofluorinated compounds having at least six fluorine atoms are conveyed to an additional reaction step to increase the number of fluorine atoms present.

Example 10: Separation of Fluorinated Compounds:

The containers of crude $C_3Cl_2F_6$ from various production runs of Steps I and II contained $C_3Cl_2F_6$ and numerous other unidentified underfluorinated compounds, and possible small amounts of H_2O, HF, Cl_2, and HCl.

Approximately 73 kg of crude $C_3Cl_2F_6$ were fed from a heated cylinder to a 57 liter Halar® lined scrubber tank. The scrubber tank contained a level gauge and an external heat tracing with a skin temperature thermocouple. The feed line into the tank was through a dip tube.

The tank was initially filled with a 5% KOH/water solution and the temperature of the tank was heated to 50°C. The mixture separated into three phases: an upper, primarily gaseous phase; a top liquid, primarily aqueous phase; and a bottom primarily organic phase. The top gas phase was removed as a vapor stream and fed to a Halar® lined scrubber. The vent gas was open to a molecular sieve dryer bed which fed into a chilled collection cylinder on a scale. Upon completion of the scrubbing of the $C_3Cl_2F_6$, the underfluorinated organics collected from the bottom phase was approximately 9.1 kg of material. The primary components of this organic liquid were $C_3Cl_4F_4$, and $C_3Cl_3F_5$ and $C_3Cl_2F_6$.

Table 8. Results of Separation of Underfluorinated Separation According to the Present Invention

Separated Phase	Constitutents
Vapor	Essentially pure $C_3Cl_2F_6$
Bottom	~6% $C_3Cl_2F_6$ and ~94% underfluorinated compounds

As table 8 demonstrates, underfluorinated compounds can be efficiently separated from $C_3Cl_2F_6$ according to the present invention.

As shown in Fig. 5, the present invention provides a third reaction step (Step III) for the selective fluorination of $C_3Cl_2F_6$ to CFC-217ba. The predominant reaction occurring in this step is as follows: $C_3Cl_2F_6 + HF \rightarrow CF_3\text{-}CFCl\text{-}CF_3 + HCl$

Preferably, Step III proceeds in the gas phase with excess anhydrous HF over a metal containing catalyst. According to one embodiment of the present invention,

hydrodehalogenation reaction products include HFC-227ea. A reaction of this embodiment is shown below:

$$C_3ClF_7 + H_2 \rightarrow \text{HFC-227ca} + HCl$$

A slight molar excess of H_2 can be used if desirable but is not necessary. The H_2:halogenated organic compound molar ratio is in the range of about 0.2:1 to about 10:1, optimally about 1.2:1.

Referring now to Fig. 6, the hydrodehalogenation is performed in fixed bed reactor 42 containing a suitable catalyst, such as palladium on a refractory oxide support, such as alumina or other suitable supports, in which case the reactor is operated at a temperature of about 30°C to about 275°C, and preferably at about 185°C. Alternatively, a ferric chloride ($FeCl_3$) catalyst on a solid support, such as active carbon can be used in which case the reactor is operated at a temperature of about 200°C to about 600°C, and preferably at about 450°C to about 500°C.

The pressure in reactor 42 should be in the range of about 1.2 Pa to about 15 Pa, and preferably about 7.9 Pa. The reaction is largely insensitive to pressure in the range of 0.9 – 7.9 Pa, however, reaction selectivity is slightly favored by lower pressures. Residence time in reactor 42 should be in the range of about 10 seconds to about 90 seconds, and preferably about 15 to about 60 seconds.

While any hydrodehalogenation catalyst could be used, the most active catalysts, such as Pt and Pd, are good selections because, in addition to the desired products, they lead to the addition of hydrogen across any double bond present or to the substitution of hydrogen for chlorine. Catalysts which may be utilized include, as charged to the reactor, common hydrogenation catalysts such as Cu, Ni, Cr, Ru, Rh or combinations thereof. It is not critical whether the catalysts are supported or not. However, supports which are unreactive to halocarbons, HF, and oxygen at hydrogenation temperatures up to 100°C higher such as metal fluorides, carbon, and titanium, may be used.

Referring now to Fig. 7, the high cost of noble metals led to concerns regarding catalyst lifetime. Initial testing demonstrated that the catalyst is somewhat fragile with activity dropping off within 5 days. Fortunately, it has been discovered that the addition of a small amount of water to the reaction stream extended catalyst lifetime. The addition of water allows the catalyst to perform in excess of 15 days.

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As Table 21 demonstrates, the present invention can be used to even further reduce the content of the undesired isomer. It is contemplated that once reduced the more isomerically pure reaction product can be recycled or further refined.

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What is claimed is:

1. A process for producing $CF_3CCl_2CF_3$ comprising:

contacting a C-3 reactant comprising one or more of perhydrogenated or partially halogenated C-3 hydrocarbons with Cl_2 and HF in the presence of a first catalyst at a first temperature to form a C-3 product comprising a C-3 perhalogenated compound, wherein the first catalyst comprises chromium and the first temperature is less than 450°C; and

contacting the C-3 product with HF in the presence of a second catalyst at a second temperature different from the first temperature to form $CF_3CCl_2CF_3$, wherein the second temperature is greater than 300°C.

2. The process of claim 1 further comprising contacting the $CF_3CCl_2CF_3$ with HF in the presence of a third catalyst to form $CF_3CClFCF_3$.

3. The process of claim 2 further comprising contacting the $CF_3CClFCF_3$ with H_2 in the presence of a fourth catalyst to produce CF_3CFHCF_3.

4. The process of claim 3 further comprising, during the contacting of the $CF_3CClFCF_3$ with H_2, contacting the fourth catalyst with water.

5. The process of claims 1, 2, 3, or 4 wherein the first temperature is from 150°C to less than 450°C and the second temperature is less than 550°C.

6. The process of claims 1, 2, 3, or 4 wherein the first temperature is at least 220°C and the second temperature is at least 470°C.

7. The process of claims 1, 2, 3, or 4 wherein, during the contacting of the C–3 reactant with the HF and the Cl_2, a molar ratio of the HF to the Cl_2 is from 0.75:1 to 8:1.

8. The process of claims 1, 2, 3, or 4 wherein, during the contacting of the C–3 reactant with the HF and the Cl_2, a molar ratio of the HF to the Cl_2 is at least 4:1.

9. The process of claims 1, 2, 3, or 4 wherein, during the contacting of the C–3 reactant with the HF and the Cl_2, a molar ratio of the Cl_3 to the C-3 reactant is from 8:1 to 10:1.

10. The process of claims 1, 2, 3, or 4 wherein the second catalyst comprises chromium and a catalyst support.

11. The process of claim 2, 3, or 4 wherein the contacting the $CF_3CCl_2CF_3$ with HF in the presence of a third catalyst occurs at a temperature of at least 200°C.

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12. The process of claims 2, 3 or 4 wherein, during the contacting of the C-3 product with the HF, a molar ratio of the HF to the C-3 product is at least 30:1.

13. The process of claims 2, 3, or 4 where during the contacting of the $CF_3CCl_2CF_3$ with the HF, a molar ratio of the HF to the $CF_3CCl_2CF_3$ is at least 10:1.

14. The process of claims 2, 3, or 4 wherein the third catalyst comprises chromium and a catalyst support.

15. The process of claim 3 or 4 wherein the contacting the $CF_3CClFCF_3$ with H_2 in the presence of a fourth catalyst occurs at a temperature of at least 30°C.

16. The process of claims 3 or 4 wherein, during the contacting of the $CF_3CClFCF_3$ with the H_2, a molar ratio of the H_2 to the $CF_3CClFCF_3$ is at least 1.2:1.

17. The process of claim 3 or 4 wherein the fourth catalyst comprises palladium and a catalyst support.

18. The process of claim 4 wherein the water is present in an amount from 0.04 to 12 percent by weight of the $CF_3CClFCF_3$.

19. The process of claim 20 wherein the amount is 0.8 percent by weight of the $CF_3CClFCF_3$.

20. A hydrogenation process comprising contacting a compound with a catalyst in the presence of water to form a hydrogenated compound.

21. The process of claim 22 wherein the contacting further comprises contacting the compound with H_2.

22. The process of claim 20 wherein a ratio of the H_2 to the compound is from 0.2:1 to 10:1.

23. The process of claims 22 or 23 wherein a ratio of the H_2 to the compound is at least about 1.2:1.

24. The process of claims 22 or 23 wherein the water is from about 0.04 to about 12 percent by weight of the compound.

25. The process of claims 22 or 23 wherein the water is at least about 0.8 percent by weight of the compound.

26. The process of claims 22 or 23 wherein the catalyst contains a metal.

27. The process of claims 22 or 23 wherein the catalyst comprises palladium and a catalyst support.

28. The process of claims 22 or 23 wherein the compound comprises C_3F_7Cl and the hydrogenated compound comprises C_3F_7H.

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29. A process for purifying CF_3CFHCF_3 comprising distilling a mixture comprising CF_3CFHCF_3, $CF_3CF_2CF_2H$, and at least one chlorofluorocarbon to form a solution comprising CF_3CFHCF_3.

30. The process of claim 31 wherein the at least one chlorofluorocarbon comprises C_3ClF_7.

31. The process of claim 32 wherein the mixture comprises a mole ratio of the chlorofluorocarbon to the CF_3CFHCF_3 of from about 0.1 to about 10.

32. The process of claim 33 wherein the mixture comprises a mole ratio of the chlorofluorocarbon to the CF_3CFHCF_3 of at least about 1:2.

33. A process for purifying chlorofluorinated compounds comprising:

providing a reaction product comprising HCl, HF, and a C-3 chlorofluorinated compound;

phase separating the reaction product into a gas phase comprising the HCl, a top liquid phase comprising the HF, and a bottom liquid phase comprising the C-3 chlorofluorinated compound; and

removing the bottom liquid phase to form a solution comprising the C-3 chlorofluorinated compound.

34. The process of claim 35 wherein the C-3 chlorofluorinated compound comprises C_3F_7Cl.

35. The process of claim 36 wherein the phase separating comprises altering the reaction product temperature to a temperature of from about 20°C to about 75°C.

36. The process of claim 37 wherein the temperature is about 25°C.

37. A process for purifying reaction products comprising:

providing a reaction product comprising HF and at least one C-3 chlorofluorinated compound;

phase separating the reaction product into a top liquid phase comprising HF and a bottom liquid phase comprising the at least one C-3 chlorofluorinated compound; and

physically separating the top and bottom phases to form a solution comprising the at least one C-3 chlorofluorinated compound.

38. The process of claim 39 wherein the C-3 chlorofluorinated compound comprises a C-3 chlorofluorinated compound having at least six fluorine atoms.

39. The process of claim 40 wherein the phase separating comprises altering the reaction product temperature to a temperature of from about -30°C to about -10°C.

40. The process of claim 41 wherein the temperature is about -20°C.

41. A process for separating chlorofluorinated compounds comprising:

providing a first solution comprising both first and second C-3 chlorofluorinated compounds, the first compound having at least six fluorine atoms and the second compound having less than six fluorine atoms;

preparing a mixture comprising the first solution and water;

phase separating the mixture into at least three phases; a gas phase comprising the first compound, an upper liquid phase comprising the water, and a lower liquid phase comprising the second compound; and

removing the gas phase from the upper and lower liquid phases to form a second solution comprising the first compound.

42. The process of claim 43 wherein the mixture further comprises a basic compound.

43. The process of claims 43 or 44 wherein the basic compound comprises KOH.

44. The process of claims 43 or 44 wherein the first compound comprises $C_3F_6Cl_2$ and the second compound comprises $C_3F_5Cl_3$.

45. The process of claims 43 or 44 wherein the first compound comprises $C_3F_6Cl_2$, and the second compound comprises $C_3F_5Cl_3$ the phase separating comprises altering the first solution reaction temperature to a temperature of from about 25°C to about 75°C.

46. The process of claims 43 or 44 wherein the first compound comprises $C_3F_6Cl_2$ and the second compound comprises $C_3F_5Cl_3$ the phase separating comprises altering the first solution reaction temperature to a temperature of about 50°C.

47. A process for purifying chlorofluorinated compounds comprising:

providing a first mixture comprising both first and second isomers of a C-3 chlorofluorinated compound, the first mixture having a first ratio of the first isomer to the second isomer; and

contacting the mixture with a catalyst to form a second mixture comprising a second ratio of the first isomer to the second isomer, wherein the first ratio is less than the second ratio.

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48. The process of claim 49 wherein the contacting further comprises heating the mixture to a temperature of from about 250°C to about 350°C.

49. The process of claim 49 wherein wherein the contacting further comprises heating the mixture to a temperature of about 280°C

50. The process of claim 49 further comprising separating at least a portion of the first isomer from the second mixture wherein the separating comprises distilling the second mixture to form a solution comprising the portion of the first isomer.

51. The process of claims 49, 50, 51 or 52 wherein the C-3 chlorofluorinated compound comprises $C_3F_6Cl_2$, the first isomer comprises $CF_3CCl_2CF_3$, and the second isomer comprises $CF_3CClFCF_2Cl$.

52. The process of claims 49, 50, 51 or 52 wherein the C-3 chlorofluorinated compound-comprises C_3F_7Cl, the first isomer comprises $CF_3CClFCF_3$, and the second isomer comprises $CF_3CF_2CF_2Cl$.

53. The process of claims 49, 50, 51 or 52 wherein the catalyst comprises chromium.

54. A process for halogenating compounds comprising:

providing a first mixture comprising both first and second isomers of a hydrofluorinated compound, the first mixture having a first ratio of the first isomer to the second isomer; and

contacting the mixture with a halogenating agent to form a second mixture having a second ratio of the first isomer to the second isomer, the first ratio being less than the second ratio.

55. The process of claim 56 further comprising separating at least a portion of the first isomer from the second mixture wherein the separating comprises distilling the second mixture to form a solution comprising the portion of the first isomer.

56. The process of claim 56 further comprising contacting the mixture with the halogenating agent in the presence of a catalyst.

57. The process of claims 56, 57 or 58 wherein the hydrofluorinated compound comprises C_3F_7H, the first isomer comprises CF_3CFHCF_3, and the second isomer comprises $CF_3CF_2CF_2H$.

58. The process of claims 56, 57, or 58 wherein the contacting comprises heating the mixture to a temperature of from about 200°C to about 350°C.

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59. The process of claims 56, 57, or 58 wherein the contacting comprises heating the mixture to a temperature of at least about 300°C.

60. The process of claims 56, 57, or 58 wherein the halogenating agent comprises Cl_2.

61. The process of claims 56, 57, or 58 wherein the halogenating agent comprises Cl_2 and a molar ratio of the Cl_2 to the mixture is from about 0.16:1 to about 3:1.

62. The process of claims 56, 57, or 58 wherein the halogenating agent comprises Cl_2 and a molar ratio of the Cl_2 to the mixture is at least about 2.5:1.

63. The process of claims 57 or 58 wherein the catalyst comprises activated carbon.

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